Effect of solid solution treatment and nitrogenation on magnetic properties of $Sm_{2+\alpha}Fe_{17}N_x$ powders

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Effect of solid solution treatment and nitrogenation on magnetic properties of $Sm_{2+\alpha}Fe_{17}N_x$ powders

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Abstract. The effect of solid solution treatment (SST) of Sm-Fe alloys and conditions of the nitrogenation on the structure and magnetic properties of the $Sm_{2+\alpha}Fe_{17}N_x$ ($\alpha = 0 \div 0.6$) powders has been investigated. It is observed that the nitrided powders with the best hysteresis properties can be prepared from the $Sm_{2.4}Fe_{17}$ alloy after the SST at a temperature of 1050°C (5 h) and heat treatment at 525°C in a H_2: N_2 = 1: 1 gas mixture with a pressure of 2.5 atm. The additional ball milling of the powder enhances the coercivity to 6.4 kOe.

1. Introduction

Since their discovery [1], the $Sm_2Fe_{17}N_x$ compounds have attracted attention because of the high values of their Curie temperature T_C, anisotropy field H_a, and room-temperature saturation magnetization $4\pi M_s$ i.e., 475°C, 250 kOe, and 15.7 kG, respectively. The interstitial nitride $Sm_2Fe_{17}N_x$ compounds are prepared via the gas-solid phase nitrogenation of the Sm_2Fe_{17} powder, ground to an average particle size of several units or tens of micrometers. The diffusion of nitrogen atoms occurs at a temperature of 350–550°C and at N_2 pressure in the range from 0.01 to tens of atmospheres as follows [2]:

$$1/2xN_2 + Sm_2Fe_{17} \rightarrow Sm_2Fe_{17}N_x \quad (1)$$

At the same time, at a temperature above 450°C, the enhanced diffusion of Fe atoms initiates the thermal decomposition of the $Sm_2Fe_{17}N_3$ nitride, as follows:

$$Sm_2Fe_{17}N_3 \rightarrow 2SmN + Fe_4N + 13Fe \quad (2)$$

Preparation of high-quality $Sm_2Fe_{17}N_x$ powders involves several technological problems. The first task is to obtain a single-phase Sm_2Fe_{17} alloy. Since the Sm_2Fe_{17} compound forms via the peritectic reaction of primary Fe crystals with a liquid enriched in Sm, solidification of the melt inevitably ends with the formation of a multiphase system containing α-Fe, Sm_2Fe_{17}, $SmFe_3$, and $SmFe_2$. The subsequent nitriding of such a multiphase system leads to the formation of numerous magnetically soft nuclei of magnetization reversal, which significantly decreases the hysteresis properties. Only prolonged solid solution treatment (SST) of ingots at temperatures below 1280°C helps removing additional phases. Samarium rapidly evaporates in the course of melting and SST of the alloys, because of its high vapor pressure. The loss of samarium can be counteracted by having its excess content in the original $Sm_{2+\alpha}Fe_{17}$ alloys. The value of the excess α is selected empirically, taking into account the melting, SST and nitrogenation, thus to ensure the formation of the single-phase $Sm_2Fe_{17}N_x$ powder.

Another crucial task for the production of highly anisotropic $Sm_2Fe_{17}N_x$ powders is the optimization of the nitriding process. The problem originates from both the low diffusion mobility of nitrogen atoms in the Sm_2Fe_{17} lattice and the instability of the $Sm_2Fe_{17}N_x$ nitride resulting in its decomposition into α-Fe and SmN [3]. Despite the wide range of studies of the diffusion of the nitrogen atoms into the rhombohedral lattice of the Sm_2Fe_{17} compound [4-15], the practical task of synthesizing the anisotropic single-phase $Sm_2Fe_{17}N_x$ powder can be reduced to optimization of the multiparameter nitrogenation for the specific conditions of its realization [16-19].

In this work, we studied the effect of SST of Sm-Fe alloys and the conditions of the nitrogenation on the structure and magnetic properties of the $Sm_{2+\alpha}Fe_{17}N_x$ nitrides ($\alpha = 0 \div 0.6$) powders.

2. Experimental

The initial $Sm_{2+\alpha}Fe_{17}$ (α=0÷0.6) alloys were prepared by the induction melting in a vacuum furnace. The alloys were subjected to the SST at 1000-1100ºC for 1-20 h. Nitrogenation of the powders was carried out at 450-550ºC for 4 h in the $H_2 + N_2$ gas mixture under pressure of up to 2.5 atm. The Curie temperatures were determined from the first derivatives of the temperature dependences of magnetic susceptibility $\chi(T)$, which were measured by the method of compensated transformer in an alternating magnetic field with an amplitude of 4 Oe and frequency of 800 Hz in the temperature range of 18–800ºC. Magnetization-reversal curves of the nitrogenated powders which were prior aligned in the magnetic field of 10 kOe were measured along and perpendicular to the texture direction using a vibrating sample magnetometer (VSM, Lake Shore 7407) with the maximum field of 17.5 kOe. X-ray diffraction patterns were taken with an Empyrean (PANanalytical) diffractometer in CuK_α-radiation. Microstructures were observed with a Neophot 2 optical microscope.

3. Results and discussion

3.1. Solid solution treatment of as-cast alloys

Figure 1 (*a* - *d*) shows the dendritic microstructure of the as-cast $Sm_{2+\alpha}Fe_{17}$ ($\alpha = 0 \div 0.6$) alloys. It consists of the matrix Sm_2Fe_{17} phase and the significant inclusions of the α-Fe and $SmFe_3$ phases (figure 1*a*). The SST at temperatures of 1000–1100°C promotes a decrease in the fraction of the α-Fe and $SmFe_3$ inclusions. Figure 2 shows the temperature dependences of magnetic susceptibility $\chi(T)$ of the $Sm_{2+\alpha}Fe_{17}$ alloys. The weak peaks at 360°C, which correspond to the Curie temperature T_C of the $SmFe_3$ phase almost completely disappear after the SST at 1000–1100ºC for 5 h. The relative contribution of the α-Fe and Sm_2Fe_{17} phases to the total susceptibility gradually increases in favor of the latter with increasing SST time. For example, only a small amount of α-Fe phase inclusions is observed in the matrix Sm_2Fe_{17} phase after the SST at 1050°C for 20 h as can be seen from the micrographs in figure 1 (*e*–*h*).

The X-ray diffraction patterns of the $Sm_{2+\alpha}Fe_{17}$ powders prepared from the alloys after the SST at 1050°C for 20 h are presented in figure 3. The alloys mainly consist of the rhombohedral modification (R-3m) of Sm_2Fe_{17} phase and the small amount of the α-Fe phase, i.e, 4.7; 10.1; 3.4 and 4.5% for α = 0; 0.2; 0.4 and 0.6, respectively.

3.2. Nitrogenation of powders

To prepare uniformly nitrided powder, it is required to carefully control the particle size, temperature, and heating time in N_2 atmosphere. In order to obtain high quality nitrides, lower temperature and longer nitrogenation time is required. Fukuno et al. [20, 21] reported that the hydrogenation before the nitrogenation significantly increased the gas-solid reaction area by inducing many cracks in the

Sm_2Fe_{17} particles. Thus, this hydrogenation promoted nitrogenation at lower temperature minimizing the impurity formation.

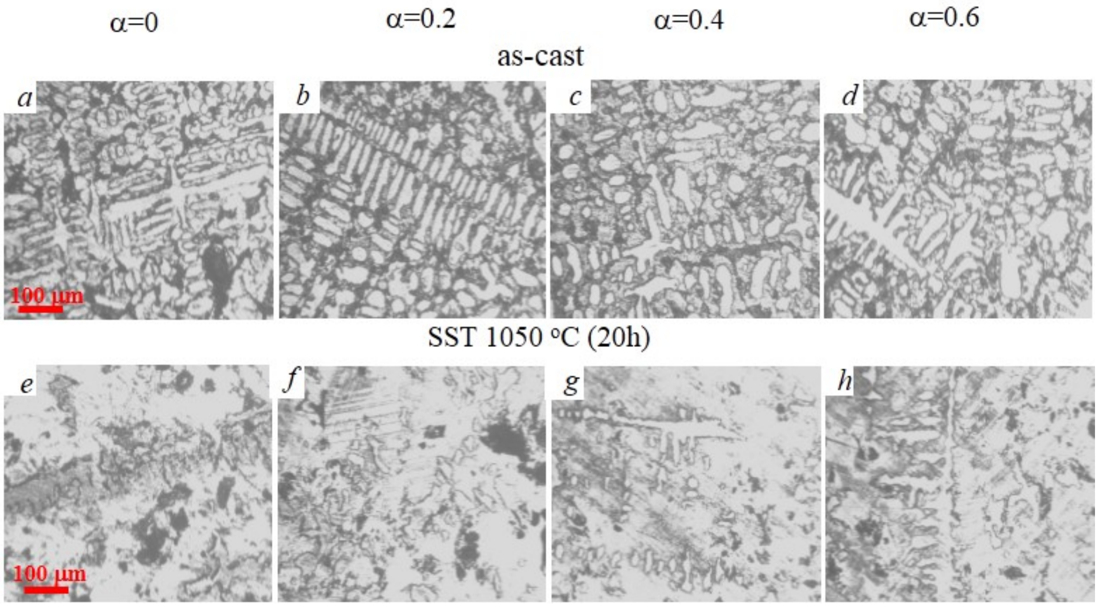

Figure 1. Microstructure of the cast $Sm_{2+\alpha}Fe_{17}$ alloys (*a-d*) before and after the SST at 1050 °C for 20 hours (*e-h*).

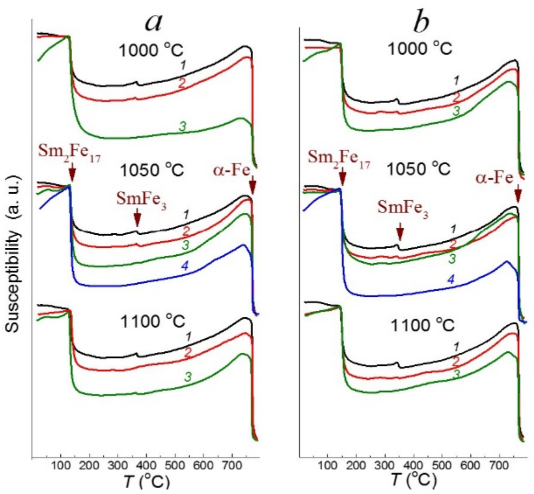

Figure 2. Temperature dependences of magnetic susceptibility of the $Sm_{2+\alpha}Fe_{17}$ alloys with $\alpha = 0$ (*a*) and $\alpha = 0.6$ (*b*) in as cast state (*1*) and after the SST at 1000, 1050, and 1100ºC for 1 h (*2*), 5h (*3*), and 20h (*4*).

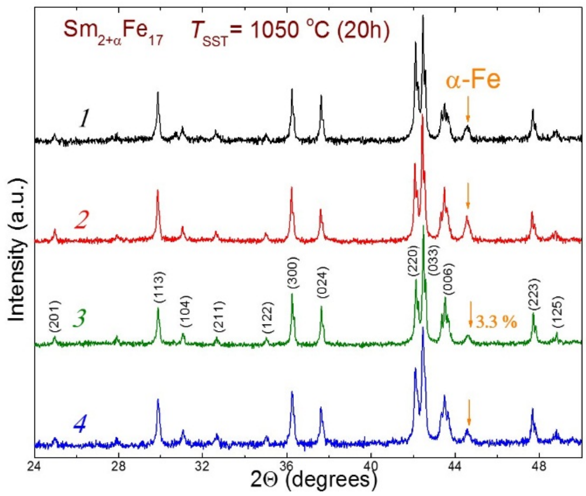

Figure 3. X-ray diffraction patterns of the $Sm_{2+\alpha}Fe_{17}$ powders after SST at 1050ºC for 20 h (*1* - $\alpha = 0$; *2* - 0.2; *3* - 0.4; *4* - 0.6).

In this work, we studied the effect of nitrogen and hydrogen ratios in the gas mixture on properties of the nitrogenated $Sm_{2+\alpha}Fe_{17}N_x$ powders. Figure 4*a* represents the temperature dependences of the ac magnetic susceptibility of the $Sm_{2.6}Fe_{17}N_x$ powders, nitrogenated at 475°C for 4 h in the H_2

and N_2 atmosphere with different H_2:N_2 ratio under the pressure 2.5 atm. The intensity of peaks in the vicinity of T_C in $Sm_2Fe_{17}N_3$ phase increased in comparison with the intensity of the Sm_2Fe_{17} peaks as H_2:N_2 ratio is equal to 1:1. Thus, as shown in figure 4*b* we obtained the largest amount of the interstitial nitrogen for $x = 2.7$. The $Sm_{2.6}Fe_{17}N_{2.7}$ powder had the maximal specific magnetization σ_{17}, which was measured in the field 17 kOe, and coercivity H_c.

The nitrogenation of $Sm_{2.6}Fe_{17}$ powder with 28 μm size particles at 475°C for 4 h did not result in the complete phase transformation from Sm_2Fe_{17} to $Sm_2Fe_{17}N_3$ as can be seen in figure 4*a*. Thus, effects of the nitrogenation temperature T_{nitr} on the properties of $Sm_{2+\alpha}Fe_{17}N_x$ (α=0÷0.6) powder was studied in detail. For example, figure 5*a* demonstrates the temperature dependences of the ac magnetic susceptibility of the $Sm_{2.6}Fe_{17}$ powders, nitrogenated at T_{nitr} = 450 – 550°C. With increasing T_{nitr} from 475 to 525°C, the relative intensity of the high anisotropic $Sm_2Fe_{17}N_3$ phase significantly increases. The Sm_2Fe_{17} phase peak gradually disappears. However, the formation of $Sm_2Fe_{17}N_x$ phase with $x < 3$ broadens the peak in the temperature range 250-350°C in the $\chi(T)$ curve. Increasing T_{nitr} up to 525 °C increases anisotropy of the magnetization measured along and across the texture direction of the powder aligned with the magnetic field (figure 5*b*).

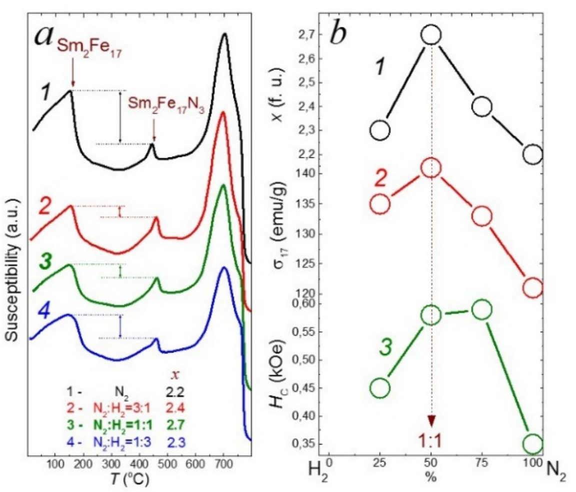

Figure 4. (*a*) Temperature dependences of the ac magnetic susceptibility of the $Sm_{2.6}Fe_{17}N_x$ powders, nitrogenated at T_{nitr}=475°C under pressure of 2.5 atm in H_2 and N_2 atmosphere with different H_2:N_2 ratio: *1* – N_2, *2* – N_2:H_2=3:1, *3* – N_2:H_2=1:1, *4* – N_2:H_2=1:3; (*b*) the effect of the H_2:N_2 ratio in the gas mixture on the amount of interstitial nitrogen *x* (*1*), magnetization σ_{17} (*2*) and coercivity H_c of the nitrogenated $Sm_{2.6}Fe_{17}N_x$ powders .

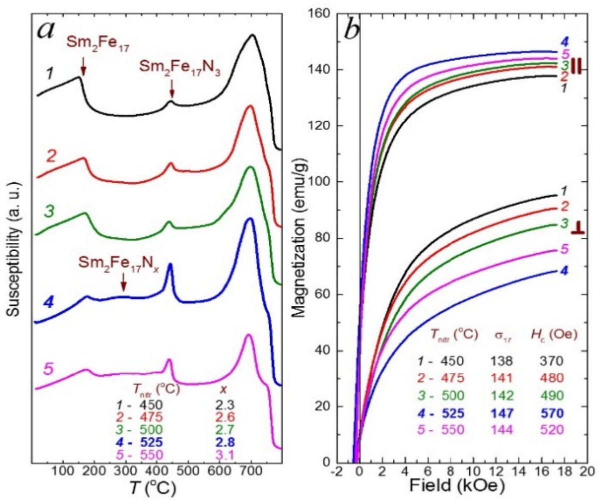

Figure 5. (*a*) Temperature dependences of the ac magnetic susceptibility, and (*b*) demagnetization curves, measured along and across alignment of textured powders, prepared from $Sm_{2.6}Fe_{17}$ alloy after SST (1100°C, 5 h) and nitrogenation at different temperature T_{nitr}: *1* - 450, *2* – 475, *3* – 500, *4* – 525, *5* – 550°C .

The dependences of properties of the $Sm_{2+\alpha}Fe_{17}N_x$ nitride with α = 0 and 0.6 on the nitrogenation temperature (450-550°C) are shown in figure 6. The amount of interstitial nitrogen *x* monotonically increases with increasing T_{nitr}. However, the values of σ_{17} and H_c reach maximum at T_{nitr} = 525°C. Further increasing T_{nitr} up to 550°C drastically decreases σ_{17} and H_c, which is caused by the accelerated decomposition of the $Sm_2Fe_{17}N_3$ nitride at elevated temperatures.

Nitrogenated powder with average grain size 28 μm and the best hysteresis properties (σ_{17} = 152 emu/g and H_c = 0.87 kOe) was obtained from the $Sm_{2.4}Fe_{17}$ alloy after annealing at 1050 °C for 5 h and subsequent heat treatment at T_{nitr}=525°C in the mixture of gases H_2:N_2 =1:1 under the pressure 2.5 atm. In order to enhance coercivity, the powder was additionally milled in a ball mill in toluene with ratio of powder to balls mass m_p/m_b = 1/15. Figure 7 represents monotonic increase of H_c up to 6.4 kOe with increasing milling time up to 24 h.

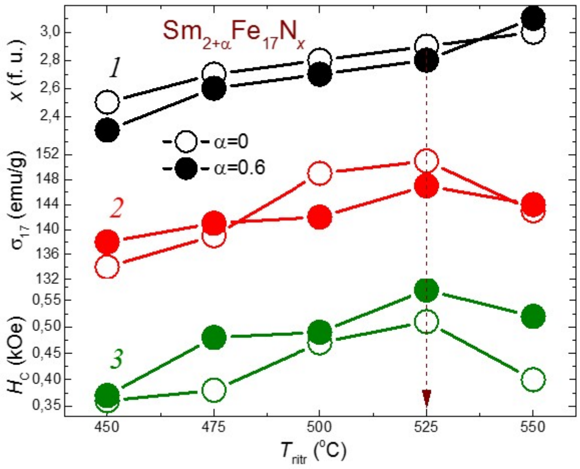

Figure 6. Dependences of the interstitial nitrogen amount x (*1*), magnetization σ_{17} (*2*) and H_c (*3*) of the Sm_2Fe_{17} and $Sm_{2.6}Fe_{17}$ powders on nitrogenation temperature T_{nitr}.

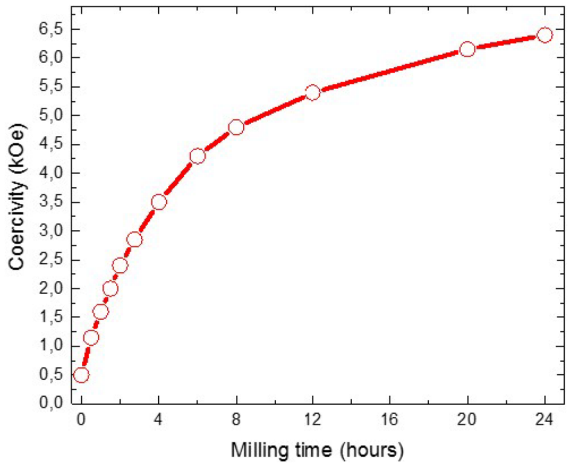

Figure 7. Effect of milling time on the coercivity of the $Sm_{2.4}Fe_{17}N_{3.4}$ powder.

4. Conclusion

By means of metallography, X-ray diffraction, measurements of the temperature dependences of the ac magnetic susceptibility and hysteresis magnetic properties of as-cast and homogenized $Sm_{2+\alpha}Fe_{17}$ (α = 0 ÷ 0.6) alloys it have been shown:

1) The addition of excess Sm with α= 0.4 to the initial $Sm_{2+\alpha}Fe_{17}$ alloys is required in order to compensate for its loss during melting and SST for 20 h at 1050 °C contributed to homogeneous starting alloy without Sm-rich phases and the minimum amount of α-Fe phase.
2) Magnetically anisotropic powder with average grain size of 28 µm and the best hysteresis properties (σ_{17} = 152 emu/g and H_c = 0.87 kOe) was prepared by nitrogenation at T_{nitr}=525°C in a mixture of gases H_2:N_2 =1:1 under pressure 2.5 atm.
3) Grinding the nitrogenated powder in a ball mill increases the coercivity up to 6.4 kOe.

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